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(54) **Cleaning composition comprising fluoro-surfactants**

(57) The invention relates to compositions for cleaning hard surfaces, wherein said composition comprises both cleans the surface and prevents or retards further soiling of the surface and provides an aqueous, hard-surface cleaning composition comprising a surfactant mixture, wherein said surfactant mixture comprises:

a) a cationic fluorosurfactant, and,

b) a non-fluorinated nonionic surfactant.

It is believed that the cationic fluorosurfactants present in the compositions of the present invention modify the surface energy of surfaces to which the composition is applied so as to raise the contact angle of soil subsequently deposited on the modified surface. Suitable fluorosurfactant compounds can be broadly described as compounds which contain at least one CF_3 moiety and a group carrying a positive charge. Preferably, the fluorosurfactants employed in the present invention are of the general formula:

$$\text{(I)} \qquad CF_3\text{-}L\text{-}N^+R_1R_2R_3$$

wherein L is a linking group which is preferably selected from linear or branched aliphatic or fluoro-aliphatic chains which may contain heteroatoms and R_1, R_2, and R_3 are preferably short chain alkyl groups, typically C1-C5 alkyl groups of which methyl groups are preferred: in an alternative, one of R_1, R_2 or R_3 is itself a moiety of the form CF_3-L-.

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Description

Technical Field

The present invention relates to compositions for cleaning hard surfaces, wherein said composition comprises both cleans the surface and prevents or retards further soiling of the surface.

Background to the Invention

In traditional cleaning of hard surfaces such as wood, glazed tiles, painted metal and the like, it is known to follow soil removal using surfactant or solvent based compositions with the application of a lacquer, wax or polish as a separate operation so as to seal and protect the surface and reduce the rate of soil redeposition. This two-step cleaning and sealing operation is both time-consuming and complex.

It has been proposed to include a range of so-called 'soil release agents', including polymers, siloxanes and quaternary cationic surfactants in cleaning compositions so as to provide a secondary cleaning benefit. It is believed that these soil release agents function by deposition of a layer of polymer, siloxane or surfactant on the surface during cleaning. This layer of material is believed to facilitate further cleaning operations by reducing the extent to which soil adheres to the surface. Obviously, some care is needed in the choice of soil-release agents as cleaning compositions typically comprise surfactants whose primary purpose is to remove materials from the surface and it is important both that the cleaning function of the composition is not impaired by the presence of the soil-release agent and that the soil release agent can deposit in the presence of surfactant.

Despite progress in this field there is a need to provide compositions which further reduce the extent to which soil adheres to surfaces and provide further formulation flexibility, especially as regards the possibility of flocculation of the compositions in the presence of electrolytes and/or other minor components.

Brief Description of the Invention

We have now devised stable compositions which both clean a surface and are believed to deposit thereupon a layer of a cationic fluorosurfactant which assists the release of soil subsequently deposited upon the said surface.

Accordingly, the present invention provides an aqueous, hard-surface cleaning composition comprising a surfactant mixture, wherein said surfactant mixture comprises:

a) a cationic fluorosurfactant, and,

b) a non-fluorinated nonionic surfactant.

It is believed that the cationic flourosurfactants present in the compositions of the present invention modify the surface energy of surfaces to which the composition is applied so as to raise the contact angle of soil subsequently deposited on the modified surface.

Typical cleaning compositions falling within the present invention comprise, in addition to nonionic surfactant, a level of cationic fluorosurfactant which is effective to lower the surface energy of a surface cleaned with the composition to below 25 mN/m.

Detailed Description of the Invention

In order that the present invention may be further understood it will be described in greater detail below with particular reference to preferred components and formulation details.

Fluoro surfactants:

It is essential that the compositions of the present invention comprise a cationic fluorosurfactant. The presence of an effective amount of the fluorosurfactant is believed to provide for the deposition of a 'protective' layer on the surface being cleaned. This layer prevents or reduces the adhesion of soil subsequently applied to the surface. The layer also causes the surface cleaned to exhibit a lower surface energy and compositions according to the invention typically reduce the surface energy to less than 25 mN/meter.

Suitable fluorosurfactant compounds can be broadly described as compounds which contain at least one CF_3 moiety and a group carrying a positive charge. We have determined that fluorosurfactants which include the CF_3 group have a larger depressive effect on the surface energy than those which include only CF_2 groups.

Typically the positive charge is borne on a nitrogen atom, and preferably the said nitrogen atom is quaternary.

Preferably, the fluorosurfactants employed in the present invention are of the general formula:

$$\text{(I)} \qquad CF_3\text{-}L\text{-}N^{+}R_1R_2R_3$$

wherein L is a linking group which is preferably selected from linear or branched aliphatic or fluoro-aliphatic chains which may contain heteroatoms and R_1, R_2. and R_3 are preferably short chain alkyl groups, typically C1-C5 alkyl groups of which methyl groups are preferred: in an alternative, one of R_1, R_2 or R_3 is itself a moiety of the form CF_3-L-.

The linking group L typically comprises a backbone which is at least six carbon or heteroatom units long. This provides sufficient spacing between the quaternary nitrogen and the $-CF_3$ group to ensure that the molecule exhibits appropriate surfactant behaviour.

Preferably L is selected from the group comprising:

$$\text{(II)} \qquad -(CF_2)_n\text{-}(CH_2)_mSCH_2CHOH\text{-}CH_2\text{-}$$

where n + m is 6-22,

$$\text{(III)} \qquad -R_4CH_2CH_2CH(R_4.CF_3)\ NHCOCH_2\text{-}$$

where R_4 is $-(CF_2)_n(CH2)_mO(CO)$- and n+m is 6 to 22,

$$\text{(IV)} \qquad -(CF_2)_n\text{-}(CH_2)_mO(CO)CH_2\text{-}CH_2\text{-}$$

where n + m is 6-22,

$$\text{(V)} \qquad -R_5CH_2CH(R_5.CF_3)CH_2\text{-}$$

where R_5 is $-(CF_2)_n(CH2)_mO(CO)$- and n+m is 6 to 22,

$$\text{(VI)} \qquad -(CF_2)_n\text{-}(CH_2)_m\text{-}$$

where n + m is 6-22,

$$\text{(VII)} \qquad -(CF_2)_n\text{-}(CH_2)_mSO_2NH(CH_2)_3\text{-}$$

where n + m is 6-22,

Particularly preferred fluorosurfactant materials are selected from the groups comprising:

$$\text{(IIa)} \qquad F_3\text{-}(CF_2)_n\text{-}(CH_2)_mSCH_2CHOH\text{-}CH_2\text{-}N^{+}R_1R_2R_3$$

where n is 5-9 and m is 2, and R_1R_2 and R_3 are $-CH_3$. A suitable material being available as ZONYL FSD (TM) ex. Dupont.

$$\text{(IIIa)} \qquad CF_3\text{-}R_4CH_2CH_2CH(R_4.CF_3)NHCOCH_2\text{-}N^{+}R_1R_2R_3$$

where R_4 is $-(CF_3)_n(CH2)_mO(CO)$-, n is 5-9 and m is 2, and R_1R_2 and R_3 are $-CH_3$. A suitable material being available as DC-5-8F2L (TM) ex. Sogo Pharmaceuticals of Tokyo.

$$CF_3\text{-}(CF_2)_n\text{-}(CH_2)_mO(CO)CH_2\text{-}CH_2\text{-}N^+R_1R_2R_3$$

where R_1R_2 are $-CH_3$ and R_3 is $CF_3\text{-}(CF_2)_n\text{-}(CH_2)_mO(CO)CH_2\text{-}CH_2\text{-}$ and n is 5-9 and m is 2. A suitable material being synthesised on request by Lancaster Synthesis Limited in Lancashire UK.

$$\text{(Va)} \quad F_3\text{-}R_5CH_2CH(R_5.CF_3)CH_2\text{-}N^+R_1R_2R_3$$

where R_1,R_2 and R_3 are $-CH_3$, R_5 is $-(CF_2)_n(CH2)_mO(CO)-$ where n is 5-9 and m is 2. A suitable material being synthesised on request by Lancaster Synthesis Limited in Lancashire UK.

$$\text{(VIa)} \quad F_3\text{-}(CF_2)_n\text{-}(CH_2)_m\text{-}N^+R_1R_2R_3$$

where n + m is 6-22 and R_1,R_2 and R_3 are $-CH_3$. Suitable materials being found in the SURFLON (TM) range of surfactants available from Asahi Glass of Japan.

$$\text{(VIIa)} \quad F_3\text{-}(CF_2)_n\text{-}(CH_2)_mSO_2NH(CH_2)_3\text{-}N^+R_1R_2R_3$$

where n is 5-9 and m is 0, and R_1R_2 and R_3 are $-CH_3$. Suitable materials are available as FLUORAD FC135 (TM) ex. Minnesota Mining and Manufacturing.

Preferred levels of cationic fluorosurfactant are the range 0.05-5%wt on product. Particularly preferred levels are in the range 0.1-2%wt on product, with levels of around 0.2%wt being most preferred as a compromise between cost and efficacy.

Nonionic Surfactants:

It is essential that the compositions of the present invention comprise a non-fluorinated nonionic surfactant. The presence of nonionic surfactant is believed to contribute significantly to the cleaning effectiveness of the compositions of the invention.

Suitable nonionic detergent active compounds can be broadly described as compounds produced by the condensation of alkylene oxide groups, which are hydrophilic in nature, with an organic hydrophobic compound which may be aliphatic or alkyl aromatic in nature.

The length of the hydrophilic or polyoxyalkylene radical which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

Particular examples include the condensation product of aliphatic alcohols having from 6 to 22 carbon atoms in either straight or branched chain configuration with ethylene oxide, such as a coconut oil ethylene oxide condensate having from 2 to 15 moles of ethylene oxide per mole of coconut alcohol; condensates of alkylphenols whose alkyl group contains from 6 to 12 carbon atoms with 5 to 25 moles of ethylene oxide per mole of alkylphenol; condensates of the reaction product of ethylenediamine and propylene oxide with ethylene oxide, the condensates containing from 40 to 80% of polyoxyethylene radicals by weight and having a molecular weight of from 5,000 to 11,000; tertiary amine oxides of structure R_3NO, where one group R is an alkyl group of 8 to 18 carbon atoms and the others are each methyl, ethyl or hydroxy-ethyl groups, for instance dimethyldodecylamine oxide; tertiary phosphine oxides of structure R_3PO, where one group R is an alkyl group of from 10 to 18 carbon atoms, and the others are each alkyl or hydroxyalkyl groups of 1 to 3 carbon atoms, for instance dimethyldodecylphosphine oxide; and dialkyl sulphoxides of structure R_2SO where the group R is an alkyl group of from 10 to 18 carbon atoms and the other is methyl or ethyl, for instance methyltetradecyl sulphoxide; fatty acid alkylolamides; alkylene oxide condensates of fatty acid alkylolamides and alkyl mercaptans.

Particularly preferred nonionic surfactants are the ethoxylated alcohols having 6-14 carbons and 2-9 moles of ethoxylation. Suitable materials include IMBENTIN 91/35 OFA (TM), a C_{9-11} nonionic having on average five moles of ethoxylation and NONIDET 91-6T (TM) a topped C_{9-11} nonionic with an average of six moles of ethoxylation.

Many more nonionic surfactants are known to the skilled worker, as set forth in M.J.Schick 'Nonionic Surfactants', Marcel Dekker (1967) and subsequent editions of the same work.

The amount of nonionic detergent active to be employed in the composition of the invention will generally be from 1 to 30%wt, preferably from 2 to 20%wt, and most preferably from 5 to 10%wt.

Anionic surfactant may be present in the composition, but is preferably present at levels of less than 1% and is more preferably absent. It is believed that the presence of anionic detergents will cause the formation of a complex between the cationic and anionic detergents which will reduce the effectiveness of the compositions.

It is particularly preferred that the ratio of nonionic surfactant to the total of anionic and cationic surfactant is such that > 75% of the total surfactant present in the composition is nonionic.

The overall surfactant content of compositions according to the present invention will generally be 1 to 30%.

Minors and other components:

A plurality of minor components can be present in the compositions of the present invention. The composition according to the invention can contain other ingredients which aid in their cleaning performance and/or improve the physical properties of the composition. These components are not essential to the functioning of the invention.

It is preferable that the compositions of the invention comprise at least 0.5%wt of an organic amine, with a pK_a of at least 8.0. This component is believed to function as ester-cleavage agent which assists cleaning of recalcitrant soils such as the pyrolised soils which are produced when fatty and/or proteinaceous foodstuffs are heated at the surface. When organic amines with a lower pK_a such as aniline are used they are ineffective in assisting cleaning.

It is preferred that the composition comprises 1-10% of an alkanolamine, with levels of 2-6%wt being particularly preferred. Particularly suitable alkanolamines include: 2-amino-2-methyl-1-propanol, mono-ethanolamine and diethanolamine. 2-amino-2-methyl-1-propanol is the most preferred organic amine.

Hydrophobic oils are optional components of compositions according to the present invention. Suitable oils include oils which rapidly dissolve triglyceride. When oils are present preferred oils include limonene, para-cymene, di-butyl ether and butyl butyrate.

A further optional ingredient for compositions according to the invention is a suds regulating material, which can be employed in those compositions according to the invention which have a tendency to produce excessive suds in use. Examples of suds regulating materials are organic solvents, hydrophobic silica and silicone oils or hydrocarbons.

Solvents are optional components of compositions according to the present invention. Where solvents are present, preferred solvents are of the form R_1-0-$(E0)_m$-$(PO)_n$-R_2, wherein R_1 and R_2 are independently C2-6 alkyl or H, but not both hydrogen, m and n are independently 0-5. More preferably, the solvent is selected from the group comprising di-ethylene glycol mono n-butyl ether, mono-ethylene glycol mono n-butyl ether, propylene glycol n-butyl ether, isopropanol, ethanol, butanol and mixtures thereof. Alternative solvents include the pyrrolid(in)ones, for example N-methyl pyrrolidinone.

Compositions according to the invention can also contain, in addition to the ingredients already mentioned, various other optional ingredients such as pH regulants, colourants, optical brighteners, soil suspending agents, enzymes, compatible bleaching agents, gel-control agents, freeze-thaw stabilisers, bactericides, preservatives, detergent hydrotropes, abrasives, perfumes and opacifiers.

It has been found convenient to deliver products according to the invention in the form of a relatively low dosage of product in a relatively fine mist. This has the significant advantage that only low levels of product need be employed. Preferably compositions according to the invention are packaged in a container adapted to produce a spray of 0.1-1.5ml of product per spraying operation, said spray having an average drop size in the range 30-300 microns.

We have determined that it is particularly advantageous to include a polymer in the compositions of the present invention so as to reduce the level of formation of exceptionally fine droplets when the composition is sprayed as a relatively fine mist. Suitable polymers include polyvinyl pyrrolidone, available in the marketplace as Polymer PVP K-90.

Suitable levels of PVP polymer range upwards from 50ppm. Levels of 300-2000ppm are particularly preferred.

Preferred compositions according to the invention comprise:

a) 0.05-5% of a cationic fluorosurfactant, and,

b) 1-30% of a nonionic surfactant.

Particularly preferred alkaline cleaning compositions according to the invention comprise:

a) 0.1-1% of cationic fluorosurfactant IIa, VIa or VIIa as described above,

b) 2-15% of an alkoxylated alcohol, nonionic surfactant, and,

c) 1-6% of an alkanolamine

Particularly preferred ne[illegible]leaning compositions according to the invention co[illegible]e:

a) 0.1-1% of a cationic fluorosurfactant as described above,
and,

b) 2-15% of an alkoxylated alcohol, nonionic surfactant.

In order that the present invention may be better understood it will be described hereinafter by way of non-limiting examples.

EXAMPLES

Aqueous compositions comprising nonionic surfactant, and a relatively low level of cationic surfactant were prepared as in Tables 1 below: using the following materials (all compositions in Table 1 are given in terms of wt% unless otherwise stated) :

NON: NONIDET 91-6T (TM: ex. Nippon Shell): a C9-C11 ethoxylated alcohol with 6 moles of ethoxylation, and topped to reduce the quantity of low ethoxylates,

IMB: IMBENTIN 91-35 OFA (TM: ex. Kolb): a C9-C11 ethoxylated alcohol with 5-6 moles of ethoxylation, and topped to reduce the quantity of low ethoxylates,

ZON: ZONYL FSD (TM) ex. Dupont,

SUR: SURFLON S121 (TM) ex. Asahi Glass of Japan,

FC1: FLUORAD FC135 (TM) ex. 3M

DC5: DC-5-8F2L (TM) ex. Sogo Pharmaceuticals,

LS1: Material (IVa) as specified above with n~7, ex. Lancaster Synthesis.

LS2: Material (Va) as specified above with n~7, ex. Lancaster Synthesis.

Solvent : Butyl Digol (TM): diethylene glycol mono n-butyl ether,

NMP N-methyl pyrrolidinone,

AMP : 2-amino-2-methyl-1-propanol,

HEQ: $[(CH_3)_3N\text{-}CH.COOR_4\text{-}CH2.COOR_5]^+Cl^-$ wherein OOR_4 and OOR_5 are fatty acid residues having a fatty acid chain length corresponding to tallow (manufactured by Hoechst).

Table 1

Ex.	Cati	Lvl (%)	Non	Lvl (%)	Post	ETh	EPh	Con	CSE
Series #1									
1	ZON	1	IMB	5	A	1639	855	49	17.4
2	ZON	0.1	IMB	5	A	4141	1738	-	-
3 *	ZON	0.01	IMB	5	A	fail	-	-	-
4	FC1	1	IMB	5	A	-	967	-	-
5*	none	-	IMB	5	A	fail	2634	<10	>25
Series #2									
6	DC5	1	IMB	5	C	87	-	74	11.2
7*	none	-	IMB	5	C	2788	-	<10	>27.6
8*	HEQ	1	IMB	5	C	364	-	38	22.2
Series #3									
9	LS1	1	IMB	5	C	78	-	-	-
10	LS2	1	IMB	5	C	99	-	-	-
11	DC5	1	IMB	5	C	87	-	-	-
12*	HEQ	1	IMB	5	C	94	-	-	-
13*	none	-	IMB	5	C	509	-	-	-
Series #4									
14*	SUR	0.01	NON	10	B	1308	-	<10	>27.6
15*	SUR	0.02	NON	10	B	1040	-	<10	>27.6
16	SUR	0.05	NON	10	B	1003	-	<10	>27.6
17	SUR	0.1	NON	10	B	473	-	<10	>27.6
18	SUR	0.2	NON	10	B	322	-	32	23.6
19	SUR	0.5	NON	10	B	221	-	31	23.7
20	SUR	1	NON	10	B	158	-	32	23.5
21*	non	-	NON	10	B	795	-	<10	>27.6

The compositions were prepared at room temperature by mixing except where HEQ was used, this latter material being dissolved in three parts propylene glycol at 70 celcius and added to water, also at 70 celcius, while stirring.

Results were obtained in four series over a period of time as it is commonly found that results should be only compared with those obtained by the same operator on the same day. These series of results are indicated as Series #1-4 in Table 1. The first five columns of table 1, give the identity of the fluoro and nonionic surfactants and their levels in the numbered examples. Examples whose number is followed by a star (*) are comparatives.

In all experiments soiled tiles were cleaned with the composition given in Table 1 and subsequently cleaned with a second composition (which did not contain the fluorosurfactant) as indicated in the column 'Post' in table 1. Compositions A-C are given below.

A- 5% IMB, 5% NMP, 3.4% AMP and 0.2Molar Na_2CO_3

B- 10% NON, 8% Solvent, 4% AMP, 1.25% K_2CO_3, 0.1% polymer (PVP K90) and 0.2% perfume.

C- 5% IMB.

In order to measure cleaning in Series #1-3, 100g dehydrated castor oil (ex. UNICHEMA) was weighed into a glass jar. To this was added 0.2g Fat Red (TM) dye (ex. SIMGA) and the mixture was stirred vigorously (2000 RPM) for 6

hours using a Heidolph stirrer. The stirred mixture was refrigerated when not in use.

In order to measure cleaning in Series #4, 100g of 1.5 poise dehydrated castor oil (ex. SEATONS) was weighed into a glass jar. To this was added 0.2g Fat Red (TM) dye (ex. SIMGA) and the mixture was stirred vigorously (2000 RPM) for 6 hours using a Heidolph stirrer. The stirred mixture was refrigerated when not in use.

In all series of examples, vitreous enamel tiles (380x300mm) were cleaned using a fresh damp J-CLOTH (TM) using, in sequence, JIF cream (TM), then a commercially available brand of hand dishwashing liquid and finally calcite powder. After drying residual calcite was removed by buffing with a paper towel.

To determine 'ETh', 1ml of the compositions listed in Table 1 was wiped onto the cleaned tiles using a fresh damp J-CLOTH. The tiles were rinsed with tap water for 15 seconds to remove excess composition and allowed to drain. Tiles were soiled over a 215x150mm area using a DeVilbiss (TM) gravity feed spray gun (MODEL MPS-514/515) using compressed air at 25 psi, by spraying from 27 cm for 35 seconds. The soiled tiles were laid horizontally in an oven at 85 Celcius and thermally aged for 1.5 hours in Series #4 and otherwise for 2.0 hours before being stored overnight. Soiled tiles were cleaned by hand using damp J-cloths and the compositions indicated in table 1. The effort required to clean the tiles is given as 'ETh' in table 1. ETh measurements are expressed in Newton.seconds, higher values indicate that more effort was required to clean the tile. Where cleaning was not possible with 2 minutes the value is given as 'fail'.

To determine 'EPh' the protocol given above was followed except the tiles were not laid in the oven but the soil was aged photochemically by exposure to daylight for 3-6 days at room temperature. The effort required to clean the tiles is given as 'EPh' in table 1. EPh measurements are expressed in Newton.seconds, higher values indicate that more effort was required to clean the tile.

The surface energy gamma$_s$/mN.m^{-1} was measured by the method of Grifalco, Good, Fowkes and Young (see Physical chemistry of Surfaces, A. A. Adamson, Wiley, New York [1990])), using the contact angle of hexadecane in Series #2 and Series #4 and dodecane in Series #1. Contact angles are given as 'Con' (in degrees) in Table 1 and calculated surface energies as 'CSE' (in mN/meter) in Table 1. For most household surfaces the surface energy after cleaning with conventional products is >25 mN/m. From the results in Series #1 of the examples it can be seen that significantly lower cleaning effort is required for compositions according to the invention than those which either contain no fluorosurfactant or only a very low and ineffective level of fluorosurfactant.

The result of the examples in Series #2 show that the same benefit is obtained for a different fluorosurfactant and that the effect obtained is better than that obtained with the non-fluorosurfactant cationic 'HEQ'.

Series #3 provides further examples illustrated with reference to the prior known cationic 'HEQ'. It can be seen that with the fluorosurfactants used essentially the same results were obtained as with the 'HEQ' material but it is believed that compositions according to the invention would not suffer from the preparation and or stability problems which have been encountered with compositions comprising the HEQ material.

Series #4 illustrates the effect of varying the level of one particular fluorosurfactant. It can be seen that for this particular material, little or no benefit is obtained at inclusion levels of below 0.05%wt but that an increasing benefit as compared with the control is found as the level of fluorosurfactant is increased.

From the examples as a whole it can be seen that the formulations of the invention in which there is a 1%wt solution of cationic fluorosurfactant give a calculated surface energy below 25 mN/m, as determined from the measurements of contact angles with hexadecane or dodecane droplets. This also demonstrates that the compositions of the invention apply an anti-resoiling benefit to surfaces cleaned with them.

Claims

1. An aqueous, hard-surface cleaning composition comprising a surfactant mixture, wherein said surfactant mixture comprises:

   a) a cationic fluorosurfactant, and,

   b) a non-fluorinated nonionic surfactant.

2. A composition according to claim 1 wherein the fluorosurfactant is of the general formula:

$$\text{(I)} \qquad CF_3\text{-}L\text{-}N^+R_1R_2R_3$$

wherein L is a linking group which is selected from linear or branched aliphatic or fluoro-aliphatic chains which optionally contain heteroatoms and R_1, R_2, and R_3 are each C1-C5 alkyl groups or one of R_1, R_2 or R_3 is itself a

moiety of the form CF_3-L

3. A composition according to claim 1 wherein linking group L comprises a backbone which is at least six carbon or heteroatom units long and L is selected from the group comprising:

$$\text{(II)} \qquad -(CF_2)_n-(CH_2)_mSCH_2CHOH-CH_2-$$

where n + m is 6-22,

$$\text{(III)} \qquad -R_4CH_2CH_2CH(R_4.CF_3)NHCOCH_2-$$

where R_4 is $-(CF_2)_n(CH2)_mO(CO)-$ and n+m is 6 to 22,

$$\text{(IV)} \qquad -(CF_2)_n-(CH_2)_mO(CO)CH_2-CH_2-$$

where n + m is 6-22,

$$\text{(V)} \qquad -R_5CH_2CH(R_5.CF_3)CH_2-$$

where R_5 is $-(CF_2)_n(CH2)_mO(CO)-$ and n+m is 6 to 22,

$$\text{(VI)} \qquad -(CF_2)_n-(CH_2)_m-$$

where n + m is 6-22, and,

$$\text{(VII)} \qquad -(CF_2)_n-(CH_2)_mSO_2NH(CH_2)_3-$$

where n + m is 6-22,

4. A composition according to claim 1 wherein the fluorosurfactant materials is selected from the groups comprising:

$$\text{(IIa)} \qquad CF_3-(CF_2)_n-(CH_2)_mSCH_2CHOH-CH_2-N^+R_1R_2R_3$$

where n is 5-9 and m is 2, and R_1R_2 and R_3 are $-CH_3$,

$$\text{(IIIa)} \qquad CF_3-R_4CH_2CH_2CH(R_4.CF_3)NHCOCH_2-N^+R_1R_2R_3$$

where R_4 is $-(CF_2)_n(CH2)_mO(CO)-$, n is 5-9 and m is 2, and R_1R_2 and R_3 are $-CH_3$,

$$\text{(IVa)} \qquad CF_3-(CF_2)_n-(CH_2)_mO(CO)CH_2-CH_2-N^+R_1R_2R_3,$$

where R_1R_2, are $-CH_3$ and R_3 is $CF_3-(CF_2)_n-(CH_2)_mO(CO)CH_2-CH_2-$ and n is 5-9 and m is 2,

$$\text{(Va)} \qquad CF_3-R_5CH_2CH(R_5.CF_3)CH_2-N^+R_1R_2R_3$$

where R_1, R_2 and R_3 are $-CH_3$, R_5 is $-(CF_2)_n(CH2)_mO(CO)-$, n is 5-9 and m is 2,

(VIa) $CF_3\text{-}(CF_2)_n\text{-}(CH_2)_m\text{-}N^+R_1R_2R_3$

where n + m is 6-22 and R_1, R_2 and R_3 are $-CH_3$, and,

(VIIa) $CF_3\text{-}(CF_2)_n\text{-}(CH_2)_mSO_2NH(CH_2)_3\text{-}N^+R_1R_2R_3$

where n is 5-9 and m is 0, and R_1R_2 and R_3 are $-CH_3$.

5. Composition according to claim 1 comprising

a) 0.05-5% of a cationic fluorosurfactant, and,

b) 1-30% of a non-fluorinated nonionic surfactant.

6. Composition according to claim 1 wherein the nonionic surfactant comprises an alkoxylated alcohol having 6-14 carbons and 2-9 moles of alkoxylation.

7. Composition according to claim 1 which comprises:

a) 0.1-1% of cationic fluorosurfactant IIa, VIa or VIIa,

b) 2-15% of an alkoxylated alcohol nonionic surfactant, and,

c) 1-6% of an alkanolamine, said composition being of pH 10-13.

8. Composition according to claim 4 which comprises:

a) 0.1-1% of a cationic fluorosurfactant, and,

b) 2-15% of an alkoxylated alcohol, nonionic surfactant,

9. Cleaning composition comprising non-fluorinated nonionic surfactant and a level of cationic fluorosurfactant which is effective to lower the surface energy of a surface cleaned with the composition to below 25 mN/m.